ARTICLE IN PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT®

ELSEVIER

Int. J. Miner. Process. xx (2003) xxx–xxx

INTERNATIONAL JOURNAL OF MINERAL PROCESSING

www.elsevier.com/locate/ijminpro

Advances in the adsorptive particulate flotation process

L.A. Féris[a], A.T. De León[b], M. Santander[c], J. Rubio[d,*]

[a] *Environmental Engineering Department, Universidade Luterana do Brasil, Miguel Tostes 101,*
CEP 92420-280, Canoas, RS, Cx. Postal 124, Brazil
[b] *Universidad Tecnológica de Panamá–Depto. de Materiales y Metalurgia, Veraguas, Panama*
[c] *Universidad de Atacama-Departamento de Ingenieria Metalúrgica-Av. Copayapi 485, Casilla 240, Copiapó, Chile*
[d] *Laboratório de Tecnologia Mineral e Ambiental–Departamento de Engenharia de Minas-PPGEM-Universidade Federal do Rio Grande do Sul. Av. O. Aranha 99-512 P. Alegre-RS-90035-190, Brazil*

Received 20 July 2001; received in revised form 12 February 2003; accepted 18 September 2003

Abstract

The removal of contaminants from liquid effluents by the adsorptive particulate flotation (APF) process, including new adsorbents and flotation devices, are reported. Herein, contaminants are adsorbed (and/or absorbed) onto the surface of a particulate carrier and both are separated attached to rising bubbles. The adsorbents were coal, charcoal, coal beneficiation tailings, modified Brazilian smectites and barite. Emulsified oils in water, dyes and metal ions present in synthetic and industrial effluents were successfully removed using various carrier and DAF, induced air flotation, IAF or jet flotation for the separation of the loaded carrier. Process efficiency was found to be a function of the carrier/contaminant mass ratio, size distribution of the carrier and system hydrodynamics. Results and mechanisms involved are discussed in terms of adsorption and flotation phenomena.

Keywords: flotation; adsorption; pollutants; alternative adsorbents

1. Introduction

Mining, metallurgical, petroleum and chemical industries generate huge amounts of wastewater usually polluted by solid powders, process chemicals, organic and other compound (Rubio, 1998; Smith, 1989). Accordingly, the search for efficient and reliable technologies to remove and control these effluents is increasing.

Different authors have proposed flotation since its application to wastewater treatment has showed technical and economical advantages (Rubio et al., 2002). The APF or carrier flotation process is a variant of the adsorbing colloid flotation process, and employs particles as carrier-sorbing (absorbing and/or adsorbing) material for the pollutants. APF resembles oxide flotation activation by metal ions, sulfide depression by anions and coal flotation with oils. Conversely, the target here is the ions, flotation reagents and oils. The carrier can be minerals, polymeric resins, activated carbon, by-products, biomass or microorganisms and must have a high surface area, high reactivity with the pollutant to be removed and good characteristics of

---

* Corresponding author.
E-mail address: jrubio@ufrgs.br (J. Rubio).
URL: http://www.lapes.ufrgs.br/Laboratorios/ltm/ltm.html.

0301-7516/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.minpro.2003.09.005

Table 1
Studies reporting the "adsorptive particulate flotation", APF process

Sorbents	Pollutants removed	References
CBT	Ni, Cu, Zn	Féris, 1998
Zeolites	Ni, Cu, Zn	Rubio and Tessele, 1997
Zeolites	Hg, As, Se	Tessele et al., 1998
Zeolites	Zn	Zouboulis et al., 1991
Pyrite	Cu, As	Zouboulis et al., 1992
Red sludge	Cu	Zouboulis et al., 1993
Dolomite	Pb	Zouboulis et al., 1993
Fly ash	Ni	Zouboulis et al., 1993
Ion exchange resin	Cu	Duyvesteyn and Doyle, 1995
Hydroxyapatite	Cd	Zouboulis et al., 1997
Activated carbon	Rhodamine B	Schneider et al., 1999
Streptomyces riomosus	Ni, Cu, Zn	Zouboulis et al., 2000
Nonliving digested activated sludge	Cd	Zouboulis et al., 2000

coagulation/flocculation and flotation (Rubio and Tessele, 1997; Zouboulis et al., 1992; Matis et al., 1989; Matis and Zouboulis, 1994; Zouboulis and Matis, 2000). Basically, the APF process includes the following stages: (a) contaminant adsorption; (b) flocculation or collector adsorption (optional) to aggregate or hydrophobize the loaded solid sorbent; (c) bubble–particle (or flocs) interactions; and (d) flotation of the loaded carrier. Several authors have proposed the removal of metal ions and others by APF process but no industrial plant has been installed yet. Table 1 summarizes some reported studies at bench and pilot scales.

This work shows advances in APF with dissolved, induced air and jet flotation to remove heavy metals ions, oils and dyes from synthetic and industrial effluents.

2. Experimental

2.1. Adsorbing materials

Petroleum adsorbing carrier: All were sized at 100% < 74 μm and added in a concentration of 625 mg l^{-1}:

- Coal fines: 18% ash content and $\rho = 1.4$ g cm^{-3}
- Coal shale: $\rho = 2.2$ g cm^{-3}
- Charcoal: $\rho = 2.5$ g cm^{-3}
- Coal beneficiation (jigging) tailing? CBT, $\rho = 2.5$ g cm^{-3}. The CBT provided by Copelmi S.A. (Rio Grande do Sul, Brazil) were sampled and grounded in a mill to 100% < 43 μm.
- Barite, very fine particles (< 74 μm) $\rho = 4.1$ g cm^{-3}

Metal ions carrier: CBT.

Dye carrier: CBT and Smectite (Bentonite). Samples of Na^+ bentonite (< 74 μm) (Paraiba, Brazil) modified with 1.1 *ortho*-phenanthroline (OP) (De Leon et al., 2001). The residual concentration of dyes was determined using spectrophotometry.

2.2. Emulsions and solutions

Petroleum emulsions: These were prepared to simulate offshore petroleum effluents, in a salty medium (NaCl) using a heavy oil, crude petroleum, having a specific gravity (ρ) of 0.933 g cm^{-3}. The droplets size distribution (100% < 20 μm) was monitored with a Malvern Sizer, Model System 3601 and residual oil concentration measured by UV spectroscopy.

Dyes: brilliant green, and methylene blue in concentrations of about 40–50 mg l^{-1}.

Heavy metal solutions: $NiSO_4 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$ and $ZnSO_4 \cdot 7H_2O$ were used for the synthetic solution using tap water. An electroplating effluent had about 90 mg l^{-1} total Zn, Ni, Cu ions (among others), a fraction being complexed with process reagents.

2.3. Flotation studies

IAF studies were performed in a Denver D-12, 1 L cell. Thus, 0.8 l of emulsion or dyes were conditioned in the same cell at 1450 rpm during 1 min, with the carrier and frother. Flotation proceeded introducing an air flow-rate of 15 l min^{-1} during 2 min while keeping system stirring. Finally, the system was allowed to stand during 5 min before sampling.

Modified jet flotation, MJF. A Jameson type cell here has been redesigned placing an internal cylinder which receive the downcomer suspension allowing all particles to enter the separation zone by the

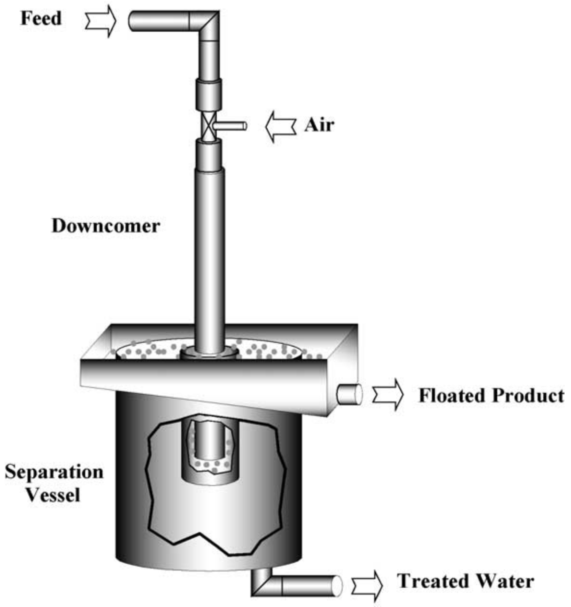

Fig. 1. Modified Jet flotation–MJF, used in the oil removal from petroleum/water emulsions (loading capacity, 25 m/h).

top. This artifact highly improved process efficiency (Fig. 1).

Dissolved air flotation (DAF) studies were conducted at bench and pilot (0.6–1 m^3 h^{-1}) scale (see Fig. 2). Process efficiency was evaluated by measuring the residual content of metal, oils, dyes and supernatant turbidity.

3. Results and discussion

3.1. Oils removal by APF-IAF

Table 2 shows results of oil separation by IAF with different oil sorbent materials. Results show that best oil sorbents were coal and CBT. Using coal, separation recovery of the oil reached 96%, yielding 19 mg l^{-1} oil content in the treated water (20 mg l^{-1}, the target). Results with CBT yielded 94% removal and 26 mg l^{-1} oil. However, after addition of a frother (16 mg l^{-1} “Dowfroth 1012”), to improve froth stability, the removal with the tailing reached 98% and only 10 mg l^{-1} in the treated water.

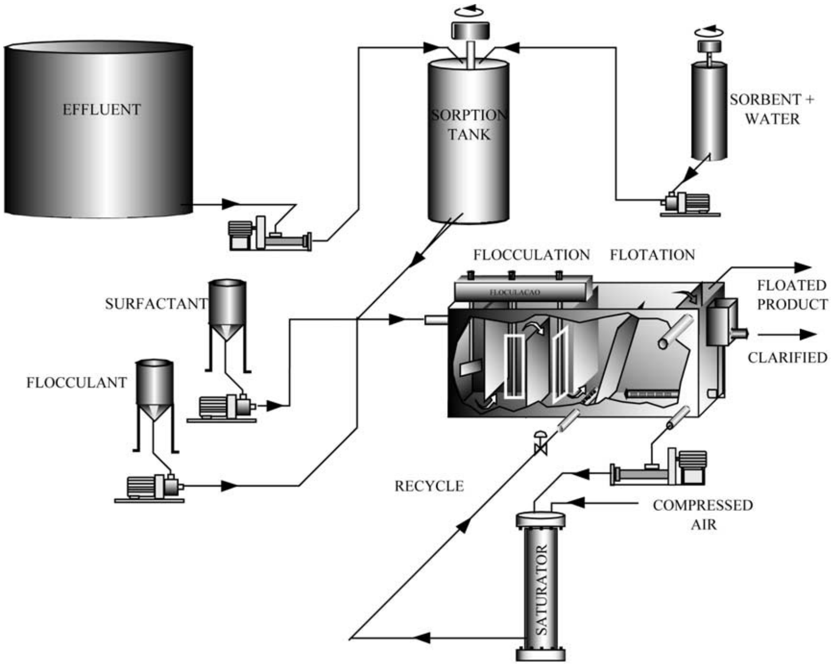

Fig. 2. Dissolved air flotation pilot unit (0.6–1 m^3/h).

Table 2
IAF results using different oil carrier: pH 6–6.5

Oil adsorbents	$(\mathrm{Oil})_i$ (mg l^{-1})	$(\mathrm{Oil})_f$ (mg l^{-1})	*R* (%)
Blank	445	105	76
Coal	440	19	96
Coal shale	478	40	92
Charcoal	476	40	92
CBT	438	26	94
CBT[a]	493	10	98
Barite	474	29	94
Barite[a]	447	29	94

$(\mathrm{Oil})_i$ and $(\mathrm{Oil})_f$ correspond to initial and final concentration of oil. R = oil removal = $\{(1-(\mathrm{Oil})_i/(\mathrm{Oil})_f)100\}$.

[a] With 16 mg l^{-1} frother ("Dowfroth 1012").

The hydrophobic adsorbents such as coal and the CBT interact with the oil droplets by hydrophobic association (forces) as in coal froth flotation. Yet, barite may adsorb the oil via chemical and/or electrostatic mechanisms between the carrier surface sites and anionic groups present in this type of oils. Eventually, silanol groups "activated" with ferric or aluminum ions, present at the surface of quartz or clays (coal cleaning tailings) may also serve as adsorption sites.

3.2. APF-jet flotation of oils

Fig. 3 shows results of removal of highly difficult-to-treat emulsified oils (petroleum) using coal as the oil carrier and a high capacity jet, continuous flotation unit. Values attained 74% oil removal yielding final oil concentrations of about 40 mg l^{-1} in one stage and using a coal/oil ratio of about 1. These results are lower than those obtained in batch IAF tests whereby most parameters are optimized. Jet type of cells, like the Jameson cells, are very rapid flotation units with very low residence time, which, in one-stage operations, are usually accompanied with short circuits or low recoveries. Yet, new upcoming devices are endowed with recycling systems to enhance residence time thus solving these recovery problems.

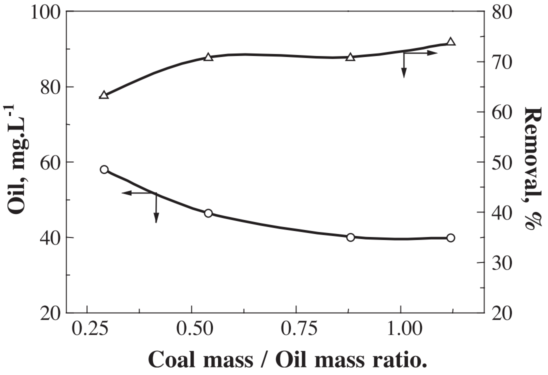

Fig. 3. Effect of the coal/oil mass ratio on modified jet flotation process efficiency $[\mathrm{oil}]_I$ = 136–158 mg.L^{-1}, frother Dowfroth–1012 = 38 mg.L^{-1}, pH 6.5.

Here, with less difficult-to-treat emulsified feeds (603 mg l^{-1} oil) and enhancing the retention time (optimal conditions), the removal was found to be normally greater than 80% regardless of the initial oil content. It is believed that this type of flotation cell has a great potential for oil or organic solvent removal at high throughput values (>25 m h^{-1}).

3.3. Removal of heavy metal ions APF-DAF (bench and pilot)

Fig. 4 shows comparative results between APF of metal-loaded CBT at bench and pilot scale and Brazilian emission limit concentration for wastewater discharge. Mechanisms involved in the sorption depend on the surface characteristics of the various compounds present in this coal tailing. Interfacial complexation between the hydrolyzed species and the negatively charged silicate surface and hydroxide precipitation at surfaces are considered the most important ones. Because of the high values of surface area, sorption capacity and price, CBT appears to have

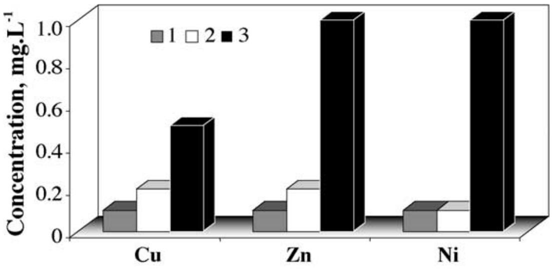

Fig. 4. Removal of heavy metals by APF–DAF process using CBT as carrier. 1–Batch scale; 2–Pilot scale; 3–Brazilian emission limit concentration.

an attractive potential as a low cost treatment of metal bearing liquid effluents.

3.4. Removal of oils, dyes and heavy metals—APF-DAF (pilot)

Fig. 5 shows the removal of oil, methylene blue and heavy metals by the APF-DAF process using CBT as carrier. Removal values higher than 85% was found for heavy metals and methylene blue and about 75% were found for oil removal.

The same figure shows that a separation efficiency of about 70% was reached for the heavy metal removal from the electroplating industrial effluent. This can be explained by the presence of other ions which also adsorb and reduce available adsorption sites and complexes which interfere and do not adsorb. Only the presence of these substances may explain the high amount of “soluble” ions and possess a huge problem for the treatment of this effluent.

3.5. Removal of dyes by APF-IAF using bentonites

Bentonites were modified with ortophenanthroline and ethylenediamine as sorbing material for oils, metal ions and dyes (De Leon et al., 2001). After this treatment, adsorption characteristics enhanced nearly 10 times, and when compared to ion exchange resins, these modified bentonites are quite similar in terms of adsorption capacity for metal ions.

In this work, the adsorption capacity for brilliant green, (BG) showed to be strongly dependent of solids concentration (MB-OP), achieving almost 100% efficiency with 1000 mg l^{-1} solid. The flotation of this loaded carrier is not straight due to the fineness, high surface area and hydrophilicity. Thus, a flocculant to reduce the number of particles (and surface area) and sodium oleate to gain hydrophobicity, were added. Best flotation results showed that IAF of dye-loaded bentonite intercalated with *ortho*-phenanthroline was successful, yielding 95–100% with the polyelectrolyte Nalco® 440C. After the addition of flocculant (only 0.2 mg l^{-1}) and the surfactant (sodium oleate, 40 mg g^{-1}) to the solution, and 1 min of mixing at 1000 rpm, the formation of flocs took place rapidly. These hydrophobic flocs adhere readily to bubbles resulting in a high flotation rate.

4. Conclusions

1. High separation values were found for oil droplets—emulsified in water by APF (IAF or jet) using mineral particles or coal wastes as carrier. Treated solutions had very low content of oil, lower than emission limits. Best carriers were

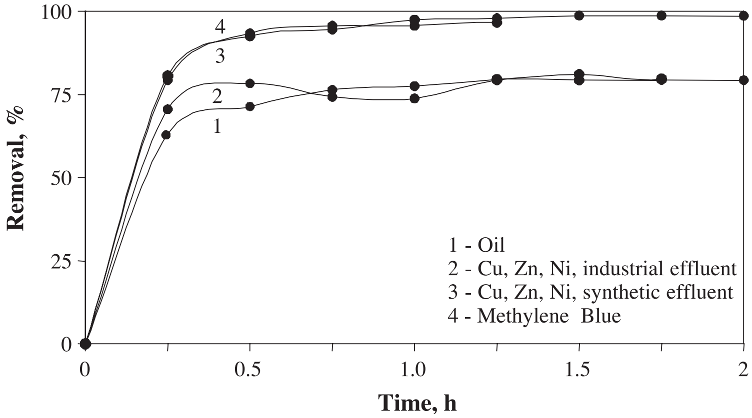

Fig. 5. Removal of pollutants by APF–DAF at pilot scale. Oil initial concentration, 1567 mg.L^{-1}; heavy metal ions concentration (synthetic effluent), 8 mg.L^{-1}; industrial effluent, 90 mg.L^{-1}; methylene blue concentration, 43 mg.L^{-1}; polyacrylamide flocculant, 0.1 mg.L^{-1}; sodium oleate, 5 mg.L^{-1}; CBT concentration, 500 mg.L^{-1}; pH 9.5; saturation pressure, 3 atm; recycle ratio, 20%.

the hydrophobic adsorbents, coal and coal beneficiation tailings.

2. The present investigation shows high removal efficiencies by APF (jet, IAF or DAF) using coal jigging tailings and modified bentonites. These carrier showed to possess good adsorbing and flotation characteristics for oils, dyes and heavy metal ions removal such as copper, zinc and nickel.

Acknowledgements

The authors are grateful to Copelmi Mineradora for the CBT samples, to the Panamanian agency SENACYT-UTP (Scholarship to A.T.De León), to PADCT/FINEP and CNPq, CAPES, UFRGS and FAPERGS (all Brazilian Agencies) for their financial support.

References

De Leon, A.T., Nunes, D.G., Rubio, J., 2001. Remoção de metais pesados em bentonitas modificadas. Proceedings: V Southern Meeting on Mineral Technology, CETEM-Rio de Janeiro, Brazil, May 30th.

Duyvesteyn, S., Doyle, F., 1995. Load and froth flotation of a chelating ion-exchange resin. In: Misra, M. (Ed.), Separation Processes: Heavy Metals, Ions and Minerals. TMS, Annual Meeting in Las Vegas, Nevada, February 12–16, pp. 123–128.

Féris, L.A., 1998. Remoção de Íons Cu, Zn e Ni por Sorção-Flotação de um Rejeito do Beneficiamento do Carvão–Processo FPS. MSc. dissertation, Universidade Federal do Rio Grande do Sul. Porto Alegre, Brazil (in Portuguese).

Matis, K.A., Zouboulis, A.I., 1994. Biosorptive flotation in metal ions recovery. Separation Science and Technology 29, 1055–1071.

Matis, K.A., Gallios, G.P., Zouboulis, A.I., 1989. Adsorption of fatty acids on fine mineral particles as a purification method of industrial wastewaters. Toxic environmental. Chemistry 20, 425–436.

Rubio, J., 1998. Environmental applications of the flotation process. In: Castro, S.H., Vergara, F., Sanchez, M. (Eds.), Effluent Treatment in the Mining Industry. Chapter 9. University of Concepción-Chile, pp. 335–364 (389 pp.).

Rubio, J., Tessele, F., 1997. Removal of heavy metal ions by adsorptive particulate flotation. Minerals Engineering 10, 671–679.

Rubio, J., Souza, M.L., Smith, R.W., 2002. Overview of flotation as a wastewater treatment technique. Minerals Engineering 15 (3), 139–155.

Schneider, I.A.H., Féris, L.A., Rubio, J., 1999. Remoção de corantes em efluentes do tingimento de ágatas por flotação de partículas adsorventes. Proceedings: XIX Congresso Associação Brasileira de Engenharia Sanitária, vol. 1. ABES-Associação Brasileira de Engenharia Sanitária, pp. 1079–1086. In Portuguese.

Smith, R.W., 1989. Flotation of algae, bacteria and other microorganisms. Mineral processing and extractive metallurgy. Review 4, 277–299.

Tessele, F., Rubio, J., Misra, M., 1998. Removal of Hg, As and Se ions from gold cyanide leach solutions by dissolved air flotation. Minerals Engineering 11 (6), 535–543.

Zouboulis, A.I., Matis, K.A., 2000. Cd^{2+} Removal by electroflotation onto sewage sludge biomass. Proceedings: The 4th International Conference Flotation in Water and Waste Water Treatment, Helsinki.

Zouboulis, A.I., Zamboulis, D., Matis, K.A., 1991. Foam flotation of Zeolites: application for zinc ion removal. Separation Science and Technology 26, 355–365.

Zouboulis, A.I., Kydros, K.A., Matis, K.A., 1992. Adsorbing flotation of copper hydroxo precipitates by pyrite fines. Separation Science and Technology 27, 2143–2155.

Zouboulis, A.I., Kydros, K.A., Matis, K.A., 1993. Removal of toxic metal ions from solutions using industrial solid byproducts. Water Science and Technology 27, 83.

Zouboulis, A.I., Matis, K.A., Lanara, B.G., Loos-Neskovic, C., 1997. Removal of cadmium from diluted solutions by hydroxyapatite: II-flotation studies. Separation Science and Technology 32, 1755–1767.

Zouboulis, A.I., Matis, K.A., Rousou, E.A., 2000. Biosorptive flotation for metal ions recovery. Proceedings: The 4th International Conference Flotation in Water and Waste Water Treatment, Helsinki.